II.G.2 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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- University of Toledo, Toledo, OH
- National Renewable Energy Laboratory, Golden, CO
- United Solar Ovonic Corporation, Troy, MI

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Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film Si-based photoelectrodes.
- To develop and demonstrate, at the end of the 3-year project, tf-Si-based photoelectrochemical (PEC) cells with high solar-to-hydrogen efficiency, long system durability, and low plant-gate hydrogen production cost.
- To investigate and develop two types of PEC cells for efficiency and durability:
  - An immersion-type photoelectrochemical cell in which the photoelectrode is immersed in electrolyte.
  - A substrate-type photoelectrochemical cell in which the photoelectrode is not in direct contact with electrolyte.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency
(Z) Materials Durability
(AB) Bulk Materials Synthesis
(AC) Device Configuration Designs
(AD) Systems Design and Evaluation

Technical Targets

This project is focused on the development of photoelectrode materials and PEC cells that are required to achieve or exceed DOE's technical target of 8% solar-to-hydrogen efficiency and 1,000 hour durability by 2013, as stated in DOE's Multi-Year Program Plan.

Accomplishments

- Designed, constructed, and tested two large-area plasma enhanced chemical vapor deposition (PECVD) systems to deposit thin-film silicon based photoelectrodes on (a) 1 ft x 3 ft substrates; and (b) 3 ft x 3 ft substrates.
- Made numerous optimization runs for amorphous silicon photoelectrodes using the newly constructed PECVD systems.
- Tested and optimized large-area magnetron sputter deposition systems to deposit transparent, conducting, and corrosion-resistant (TCCR) coatings on 1 ft x 4 ft substrates. The system has four 4" x 15" linear sputter cathodes to deposit various metal and oxide layers.
- Fabricated improved zinc oxide and indium tin oxide materials on 1 ft x 4 ft substrates.
- Designed a large-area sputter deposition system to deposit TCCR coatings on 3 ft x 3 ft substrates. The system has four 6" x 48" linear targets to deposit various metal and oxide layers.
- Improved a photoelectrochemical shunt passivation process to remove current-leaking shunts/shorts in thin-film silicon photoelectrodes thereby improving device yield.
- Continued development of immersion-type PEC cells and substrate-type PEC cells.
- Fabricated a-Si/a-SiGe/nc-Si triple-junction and a-Si/nc-Si double-junction photoelectrodes using a small-area cluster tool deposition system.
- Continued testing of a 4" x 12" substrate-type PEC panel for hydrogen production.
- Established an environmental test facility for durability of PEC modules.

Introduction

This project is focused on the development of PEC hydrogen generation devices and systems. Two approaches are taken for the development of efficient and durable PEC cells:

1. Immersion-type PEC cells (Task 4) where the photoelectrode is immersed in electrolyte.
2. A substrate-type PEC cell (Task 5) where the photoelectrode is not in direct contact with electrolyte.

Approach

Research is carried out for both the immersion-type PEC cell and the substrate-type PEC cell. For immersion-type PEC cells, two paths are taken for the development of efficient and durable photoelectrodes. In the first path (Task 1), triple-junction tf-Si-based solar cells (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/nc-Si) are used to generate the voltage bias and a TCCR coating is deposited on top to protect the semiconductor layer from corrosion while forming an ohmic contact with the electrolyte. In the second path (Task 2), a hybrid structure in which two tf-Si based junctions (middle and bottom junctions) of the present triple-junction tf-Si cell provide a voltage bias (around 1.1 V) and a third junction (the top junction) is a rectifying junction between a photo-active semiconductor and the electrolyte.

Five technical tasks are being performed in this project toward the objectives:

- **Task 1:** Development of transparent, conducting, and corrosion resistant coating for triple-junction tf-Si based photoelectrodes.
- **Task 2:** Development of hybrid multijunction PEC electrode having semiconductor-electrolyte junction.
- **Task 3:** Investigation and characterization of photoelectrochemistry.
- **Task 4:** Fabrication of low-cost, durable and efficient immersion-type PEC cells and systems.
- **Task 5:** Fabrication of low-cost, durable and efficient substrate-type PEC cells and systems.

Results

Task 1: Transparent, Conducting and Corrosion Resistant Coating for Triple-Junction tf-Si-Based Photoelectrode

The objective of this task is to develop a TCCR material that can be made at low temperature (below 250°C) using a low-cost thin-film deposition technique, having the following properties: high optical transmission in the visible wavelength range, high electrochemical stability in the electrolyte, and sufficient conductivity for transport of charge carriers, such that an ohmic contact is formed with both the electrolyte and the topmost layer of the tf-Si solar cell.

During this project period, the effort was mostly focused on the development of large-area sputter deposition system that can be used to deposit TCCR materials on large-area substrates. A deposition chamber (Figure 1a) capable of making TCCR coatings on 1 ft x 4 ft substrates was restored and optimized. The system has four 4" x 15" linear targets and substrates are mounted on a turn-table rotating inside the chamber for the deposition of films from any or all of the sputter

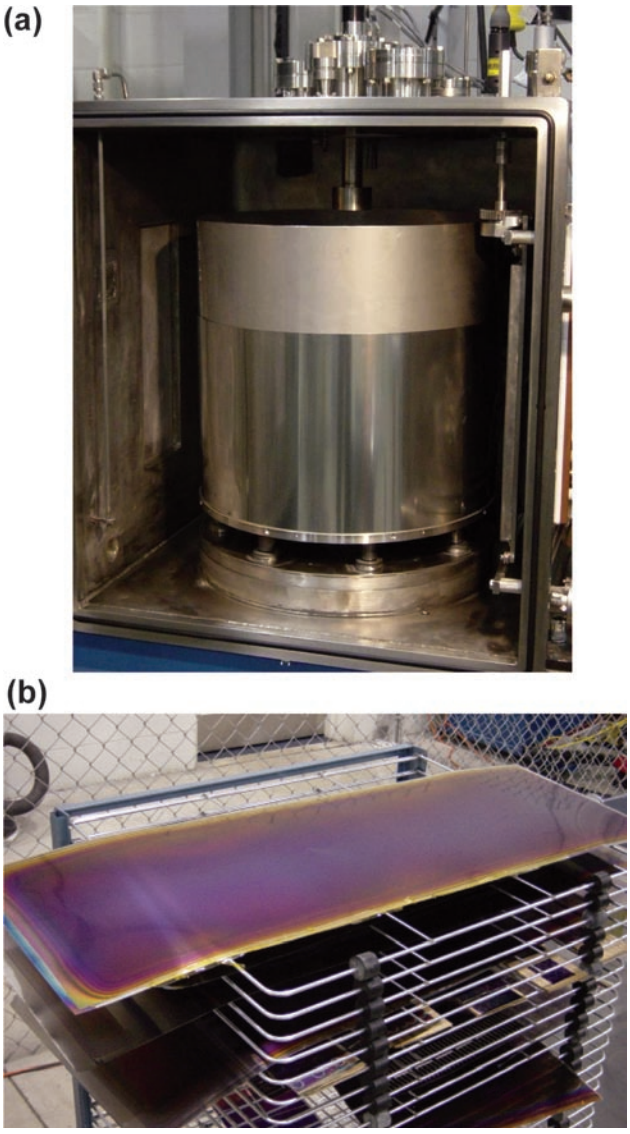

FIGURE 1. (a) Sputter System for Depositing TCCR Materials on 1 ft x 4 ft Substrates; (b) Amorphous Silicon Photoelectrodes Coated with Indium Tin Oxide – a Transparent Conductor

targets. Numerous oxide materials including ZnO and indium-tin oxide (ITO) coatings were deposited using this newly restored sputter system (Figure 1b).

Task 2: Hybrid Multijunction PEC Electrode Having Semiconductor-Electrolyte Junction

The objective of this task is to develop a photoactive semiconductor (PAS) material that 1) is stable in electrolyte both in dark illuminated conditions; 2) forms a high-quality rectifying junction with electrolyte and an ohmic contact with the tf-Si layer underneath; 3) generates at least 7.5 mA/cm^2 current so that it can be matched with the middle and bottom component solar cells in a tf-Si based triple-junction stack; and 4) is deposited at low temperature (< 250°C) using a low-cost deposition method.

During this project period, deposition facilities for making photoactive semiconductor materials were established and various photoactive semiconductor materials were explored. Additionally, double-junction thin-film silicon photoelectrodes were fabricated. Figure 2 shows the performance (I-V in Figure 2a and quantum efficiency in Figure 2b) of a double-junction photoelectrode with amorphous silicon top cell and nanocrystallline silicon bottom cell. Such a cell could be used, in conjunction with a photoactive semiconductor, to form a triple-junction photoelectrode with sufficient voltage to split water.

Task 3: Investigation and Characterization of Photoelectrochemistry

This task is focused on the characterization of PEC materials and devices. Activities during the project period involved setting up an environmental test chamber (Figure 3a and Figure 3b) that will be used to perform durability test of PEC panels.

Task 4: Fabrication of Low-Cost, Durable and Efficient PEC Cells and Systems

The objective of this task is to fabricate and optimize immersion-type PEC cells and systems. Major accomplishments under this task include:

- Optimization of a large-area PECVD system capable of making triple-junction and double junction tf-Si photoelectrodes on large-area (1 ft x 3 ft) substrates (Figure 4a).
- Design, construction and optimization of a large-area plasma-enhanced chemical vapor deposition (PECVD) system capable of making triple-junction and double-junction tf-Si photoelectrodes on large-area (3 ft x 3 ft) substrates (Figure 4b).
- Fabrication of large-area thin-film Si photoelectrodes (Figure 4b). The design of the system has been improved during the period to provide uniform deposition in large areas.

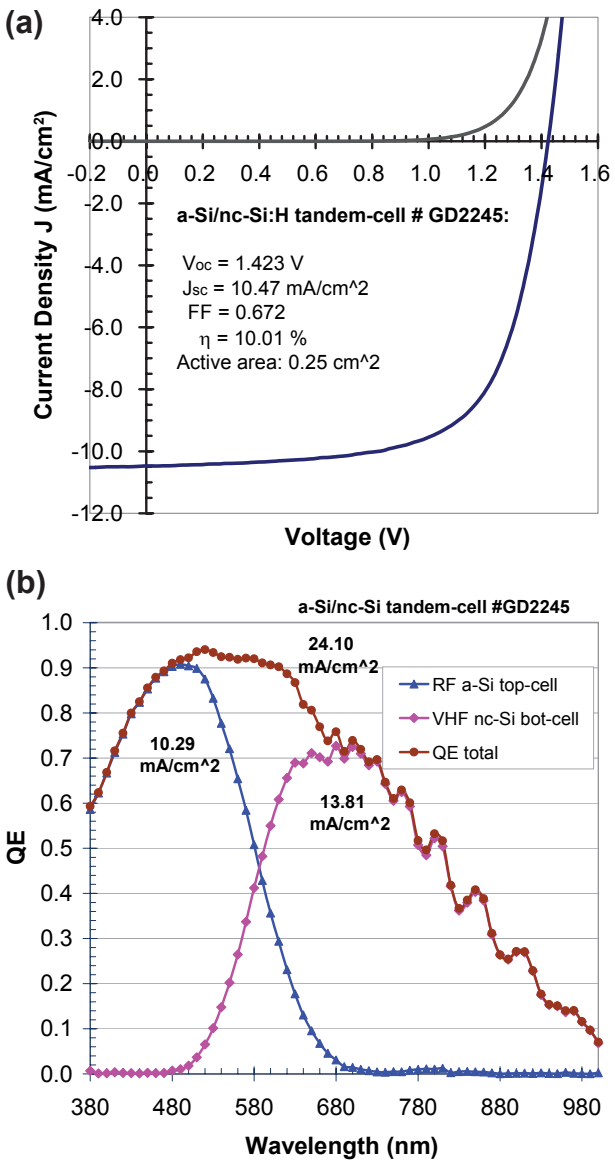

FIGURE 2. (a) Current-Voltage Characteristics of a Double-Junction Photoelectrode Showing 10% Conversion Efficiency; (b) Quantum Efficiency Curves of a Double-Junction Potoelectrode Having a-Si Solar Top Junction and Nanocyrstalline Silicon Bottom Junction

The equipment construction is paid for using funding from the State of Ohio (Ohio Department of Development) and from private investment as cost share to this DOE project. These deposition systems (Figure 4a and Figure 4b) can be used to deposit photoelectrodes with conventional type structures (light entering p-layer) and revised structures (light entering n-layer), as both may be required for photoelectrodes for various electrode designs.

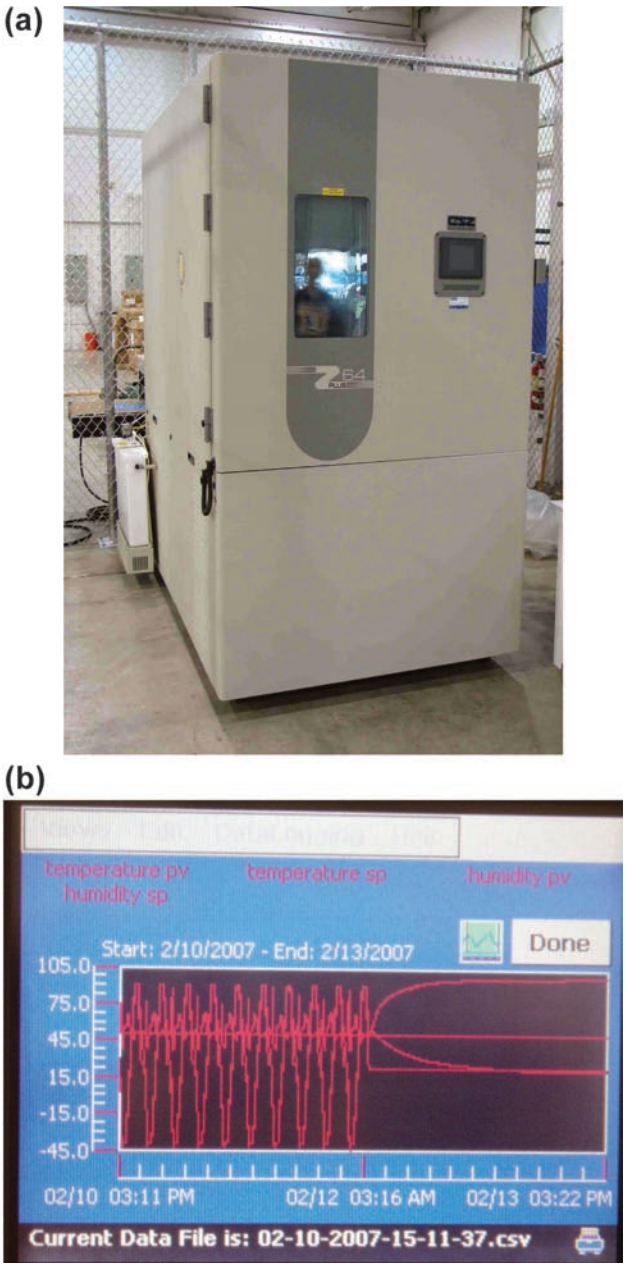

FIGURE 3. (a) Environmental Chamber Capable of Testing Durability of PEC Panels; (b) Display of the Environmental Chamber Showing Thermal Cycling Test

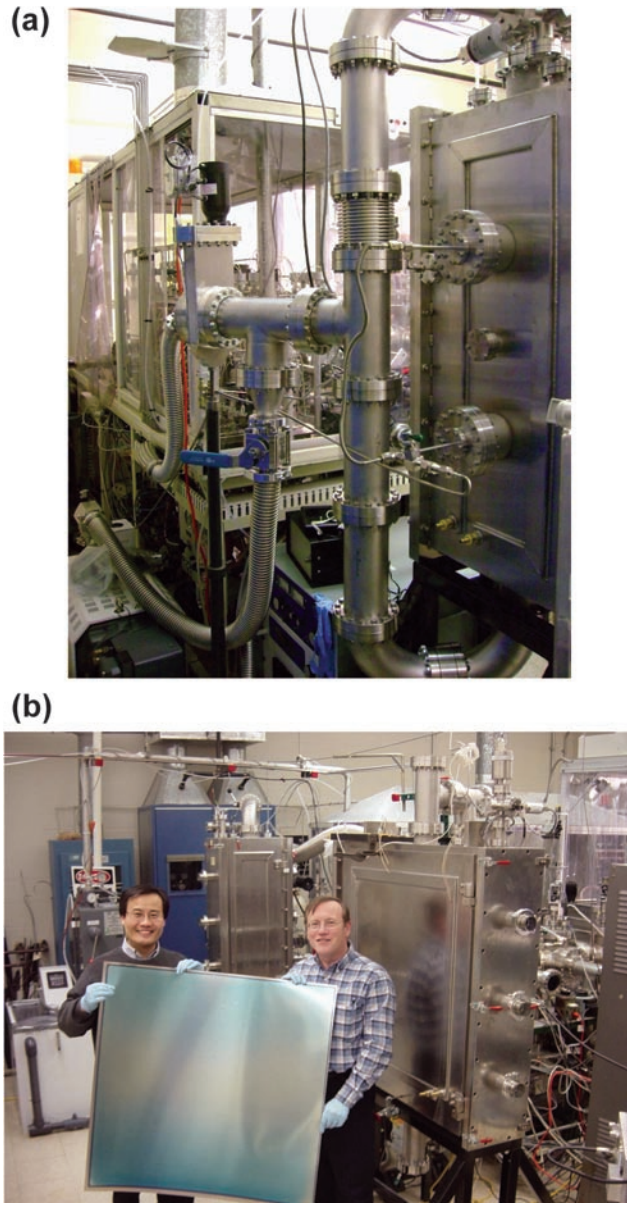

FIGURE 4. (a) PECVD Chamber Capable of Making 1 ft x 3 ft Photoelectrodes; (b) Newly Constructed PECVD Chamber Capable of Making 3 ft x 3 ft Thin-Film Silicon Photoelectrodes

Task 5: Fabrication of Low-Cost, Durable and Efficient Substrate Type PEC Cells and Systems

The objective of this task is to develop and improve a substrate-type photoelectrochemical cell for hydrogen generation. In such a PEC cell, a triple-junction amorphous silicon photoelectrode deposited on a conducting substrate is integrated into a PEC cell in which the hydrogen and oxygen compartments are both behind the photoelectrode and are separated by a membrane. Areas of research activities include the development of improved encapsulation materials and processes and the optimization of grid configuration and installation process. Additionally, a photoelectrochemical shunt passivation process has been further developed and optimized. In such a shunt passivation process, a photoelectrode is immersed in an $AgCl_3$ electrolyte. While the sample is exposed to light, a voltage bias is applied briefly (for a few seconds). The applied voltage bias converts ITO (or other oxide) near any shunted or shorted area, into an insulator, thereby electrically isolating such current-leaking shunts. A system capable of doing shunt passivation on a 1 ft x 1 ft sample is constructed (shown in Figure 5a) and tested.

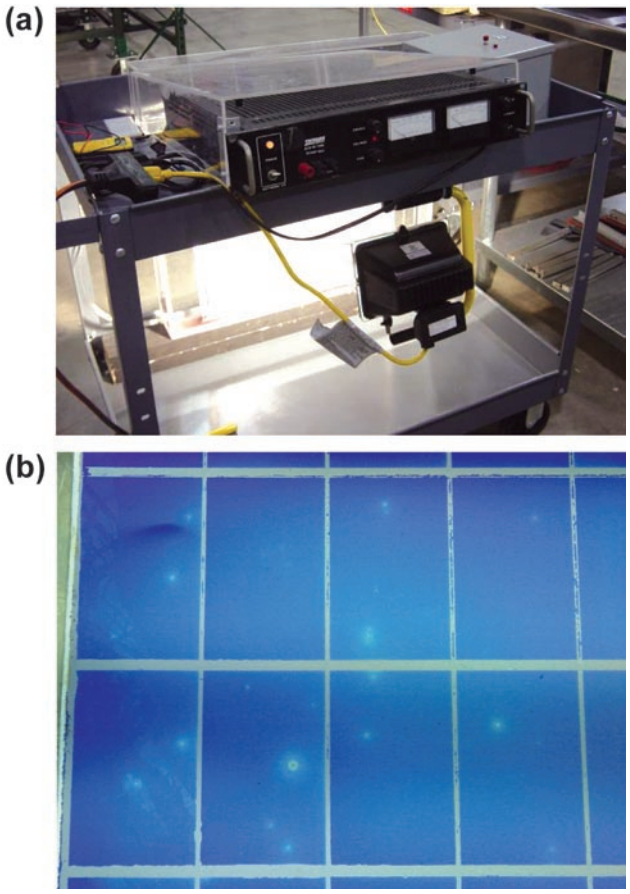

FIGURE 5. (a) PEC Shunt Passivation Process Capable of Removing Shunts and Shorts and Improving Production Yield of Photoelectrode Devices; (b) 6"x 12" Sample That Has Gone Through the PEC Shunt Passivation Process

Photoelectrodes previously shunted were recovered after the PEC shunt passivation (Figure 5b). During this period, we continued testing of substrate-type PEC panel and measured 4.3% solar-to-hydrogen conversion efficiency for a 4"x12" PEC panel.

Conclusions and Future Directions

- Demonstrated high efficiency nanocrystalline silicon-based triple-junction and double-junction photoelectrodes.
- Installed, constructed, and optimized deposition systems for the fabrication of large-area photoelectrodes with the first system making photoelectrodes on 1 ft x 3 ft substrates and the second system making photoelectrodes on 3 ft x 3 ft substrates. Uniform deposition of silicon thin films were obtained after optimization.
- Continued testing of 12 large-area (2 ft x 4 ft) PEC panels outdoors and analysis of various degradation mechanisms.
- Installed and constructed facilities capable of making large-area substrate-type PEC cells.
- Continued testing of substrate-type PEC cells (4"x12") attaining 4.3% solar-to-hydrogen conversion efficiency.

Future plans include continuation of these activities and focus on the fabrication of larger-area substrate-type PEC systems.

Special Recognitions & Awards/Patents Issued

1. PCT Patent Application, "Integrated Photovoltaic-Electrolysis Cell." Inventors: Malabala Adiga, Xunming Deng, Aarohi Vijh, and Liwei Xu. Filing No: PCT/2006/013222, April 10, 2006. Corresponds to Ser. No. 60/670,177 filed April 11, 2005.

2. PCT Patent Application, "Interconnected Photoelectrochemical Cells," entered into the national phase with country selected: U.S., May 16, 2006, PCT No. S2005/005121. Priority based on US Ser. No. 60/545,892. Inventors: X. Deng and L. Xu.

FY 2007 Publications/Presentations

1. William B. Ingler Jr., Daniel Sporar, and Xunming Deng, "Sputter Deposition of In-Fe2O3 Films for Photoelectrochemical Hydrogen Production," full papers submitted June 2006 to 210th Electrichemical Society Meeting, 2006 Joint International Meeting, Cancun, Mexico, October 26 – November 3, 2006.

2. William B. Ingler Jr., Dinesh Attygalle, and Xunming Deng, "Properties of Rf Magnetron Sputter Deposited Cobalt Oxide Thin Films as Anode for Hydrogen Generation by Electrochemical Water Splitting," full papers submitted June 2006 to 210th Electrichemical Society Meeting, 2006 Joint International Meeting, Cancun, Mexico, October 10 – November 3, 2006.